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(54) 【発明の名称】 金属粉末射出成形法によるTi系合金焼結体の製造方法

法

## (57) 【要約】

【目的】 脆性が改善されたTi系合金焼結体の製造方法の提供。

【構成】 表面をNi、Co、Cu、Ag、Au等の金属で被覆したTi粉末と有機バインダーとの混練時の最大せん断応力を $2 \times 10^5$  Pa以下かつ最大せん断応力を $2 \times 10^5$  Pa以下で射出成形し、脱脂、焼結する。

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## 【特許請求の範囲】

【請求項1】 Ti粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法によって0.05~5μmの厚さに被覆し、混練、成形、脱脂、焼結することを特徴とする金属粉末射出成形法によるTi系合金焼結体の製造方法。

【請求項2】 Ti系粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法またはメッキ法によって0.05~5μmの厚さの層に被覆したTi系粉末とバインダーとを、最大せん断応力 $2 \times 10^5$  Pa以下で混練し、かつ、最大せん断応力 $2 \times 10^5$  Pa以下で射出成形し、脱脂、焼結することを特徴とする金属粉末射出成形法によるTi系合金焼結体の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は金属粉末射出成形法によるTi系合金焼結体の製造方法に係り、詳しくは、表面をNi、Co、Cu、Ag、Auの金属粉で被覆したTi系粉末をそのまま若しくは有機バインダーと共に特定の最大せん断応力で混練し、脱脂焼結する金属粉末射出成形法による脆化性の改善されたTi系合金焼結体の製造方法に係る。

## 【0002】

【従来の技術】Ti合金は比強度が高く、しかも耐食性に優れた特性を有するため、航空機用材料や化学装置の耐食材料等に用いられている。しかしながら、鍛造や切削の加工性が劣るため、その製造方法が問題とされ、粉末冶金法によるTi合金の製造が注目されている。粉末冶金の中でも、寸法精度が優れ、複雑形状部品が製造可能な金属粉末射出成形法によるTi合金の製造に対する要望が高くなっている。

【0003】Ti合金の製造において、特に重要な点は、脆化を防ぐようにするため、炭素、酸素等の固溶元素の含有量を極力下げることにある。また、金属粉末射出成形法では金属粉末と有機バインダーを混練し、成形、脱脂、焼結というプロセスを経るが、活性なTi系粉末を用いた場合、有機バインダー中の炭素、酸素等の元素とTi系粉末が反応し、脱脂後に多量の炭素、酸素を含む。金属粉末射出成形法によるFe系合金やステンレス鋼の製造においては、焼結時の炭素と酸素の反応により、脱脂後に残留する炭素、酸素を取り除くことが可能であるが(特開平2-290901号、特開平2-54701号の各公報参照)、Ti合金においては、Tiの炭化物、酸化物が安定なため、焼結時に炭素、酸素を取り除くことは不可能であり、そのため脱脂後の炭素、酸素はそのまま焼結体中に炭素、酸素として残るといった問題があった。

## 【0004】

【発明が解決しようとする課題】本発明は上記問題を解

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決することを目的とし、具体的にはTi合金の製造において、炭素、酸素等の固溶元素含有量の増大は材料の脆化をもたらすこと、また、金属粉末射出成形法において、混練、成形、脱脂時にTi系粉末へ炭素、酸素が侵入することをそれを極力防止し、また、Ti系合金に被覆した層が後の混練や成形工程で剥離しないように所望の焼結体を製造する方法を提案することを目的とする。

## 【0005】

【課題を解決するための手段】すなわち、本発明はTi粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法によって0.05~5μmの厚さに被覆し、混練、成形、脱脂、焼結することを特徴とし、また、Ti系粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法またはメッキ法によって0.05~5μmの厚さの層に被覆したTi系粉末とバインダーとを、最大せん断応力 $2 \times 10^5$  Pa以下で混練し、かつ、最大せん断応力 $2 \times 10^5$  Pa以下で射出成形し、脱脂、焼結することを特徴とする。

【0006】以下本発明の手段たる構成ならびにその作用について詳しく説明する。

## 【0007】

【作用】本発明で使用するTi系粉末の平均粒径はコンパウンドの流動性および粉末の焼結性から0.1~100μmの範囲とすることが好ましい。さらに好ましくは平均粒径0.1~50μmの範囲である。粉末粒径は小さいほど射出時の流動性がよく、焼結性もよいので有利であるが、平均粒径0.1μm未満に微粉にするためには膨大なエネルギーを必要とするため実用上不利である。平均粒径が100μmを超えると射出成形時の流動性が悪くなるとともに、焼結性も低下し、焼結密度が上からなくなる。また、そのTi系粉末は水素化脱水素粉、ガスアトマイズ粉等のいずれの製造方法でつくられたものでよい。

【0008】被覆する金属としてはTiよりも炭素、酸素等の元素との結合が弱いNi、Co、Cu、Ag、Auを用い、これらをTi系粉末表面に0.05~5μmの厚さ被覆することにより、Ti粉末中への炭素、酸素の侵入を抑制することが可能となる。被覆の厚さが0.05μm未満では、Ti系粉末表面に均一な被覆を施すことができず、炭素、酸素が侵入し、低炭素量、低酸素量の焼結体は製造できない。また、厚さ5μmを超える被覆では、合金元素含有量の増加により材料の延性が低下し、本発明の効果はなくなる。

【0009】Ti系粉末表面上へのNi、Co、Cu、Ag、Auの群から選ばれた1種以上の金属粉の被覆方法は機械的複合法、メッキ法等、いずれの方法でもよい。機械的複合法では次のようにする。アトライター、ボールミル、振動ミル、オングミル等の粉砕機を用い、これらの粉砕機にTi系粉末および被覆粉末を投入し、

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15分から120分の被覆処理を施す。処理雰囲気は酸化防止のため、真空中、 $N_2$ 雰囲気あるいはAr等の不活性ガス雰囲気で行なうことが好ましい。添加する被覆粉末は単一種でも複數種でもよい。メッキ法では無電解メッキ、電解メッキ等いずれでもよい。

【0010】有機バインダーは金属粉末射出成形法に用いられている、公知のバインダーを使用することができる。混練は例えば加圧ニーダー、プラストミル、ロールミル、パンバリミキサー、単軸スクリュ混練機、2軸スクリュ混練機などせん断作用により混練が行なうことができる混練機を使用することができるが、これら2種以上を組み合わせる混練してもよい。混練順序は特に制限はなくいずれの順序でもよい。粉末とすべてのバインダー成分を同時に混練しても良いし、すべてのバインダー成分を先に混練後、粉末を投入して混練しても良い。また、粉末とバインダーのある成分を先に混練し、後から残りのバインダー成分を加えても良い。ただし、混練時の各混練機での最大のせん断応力 $2 \times 10^5 \text{ Pa}$ 以下となるような条件で混練を行なう。好ましいせん断応力は $1 \times 10^5 \text{ Pa}$ から $2 \times 10^5 \text{ Pa}$ である。 $1 \times 10^5 \text{ Pa}$ 未満のせん断応力では粉末とバインダーを均一に混練することができない。 $2 \times 10^5 \text{ Pa}$ を超えるせん断応力を作用させると、Ti系粉末の被覆が剥離し、炭素ならびに酸素の侵入を抑制できなくなり、炭素量ならびに酸素量の低い焼結体は製造できなくなる。混練時のせん断応力は以下のように定義される方法により測定した。すなわち、所定の混練温度、混練時間でコンパウンドを混練し、混練時に発生するせん断速度とキャピラリーレオメーターで測定された混練温度での粘度との積を混練時のせん断応力とした。

【0011】成形は一般的な熱可塑性プラスチック用射出成形機を用いて行なうことができる。射出方式はプランジャ式、プランジャブリブラ式、スクリュブリブラ式、インラインスクリュ式のいずれでもよい。ただし、予備可塑化段階あるいは射出時にコンパウンドに作用する最大のせん断応力が $2 \times 10^5 \text{ Pa}$ 以下となるような条件で射出成形を行なう。これを超えるせん断応力を作用させると、Ti系粉末の被覆が剥離し、炭素ならびに酸素の侵入を抑制できなくなり、炭素量ならびに酸素量の低い焼結体は製造できなくなる。射出成形におけるせん断応力は以下のように定義される方法により測定し

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た。すなわち、キャピラリーレオメーターで測定した射出成形温度でのコンパウンドの粘度と予備可塑化段階あるいは射出時に発生するせん断速度との積をせん断応力とした。

【0012】脱脂は酸化を防ぐために、非酸化性雰囲気中あるいは減圧中で熱分解法により脱脂するのが望ましい。焼結は非酸化性雰囲気あるいは真空中で行なう。

#### 【0013】実施例1

##### (1) 機械的複合法による実施例

10 それぞれ表1に示した平均粒径のTi粉末と被覆材となるNi、Co、Cu、Ag、Auの群から選ばれた1種以上の金属粉末を高速回転ボールミル（アトライター）に投入し、 $N_2$ 雰囲気中で回転数300rpmで60分間複合化処理を施した。粉砕ボールにはWCを用い、水冷しながら処理を行なった。被覆粉末の添加量を調整することにより、被覆材の厚さが0.03~5.8 $\mu\text{m}$ までの被覆粉末を作製した。被覆材の厚さは複合化処理を施した粉末を樹脂に埋め込み、研磨を行なった後、走査型電子顕微鏡（SEM）による粉末断面の観察結果から求めた。次に、これらの被覆粉末を熱可塑性樹脂、ワックス、可塑剤からなる有機バインダーと加圧ニーダーにより表1に示した最大せん断応力で混練し、金属粉末射出成形用コンパウンドを作製した。射出成形機によつて、このコンパウンドから $55 \times 10 \times 3 \text{ mm}$ の抗折力試験片を表1に示した最大せん断応力で成形した。成形体は窒素中で $450^\circ\text{C}$ まで48時間で昇温することにより脱脂を行ない、続いてアルゴンガス中で $1200^\circ\text{C}$ で2時間保持し、焼結を行なった。

30 【0014】比較材として、Ti粉末と同様の被覆用粉末をV型ブレンダーで混合し、同様に混練、成形、脱脂、焼結を行ない、焼結体を作製した。

【0015】以上の焼結体に対する炭素量、酸素量の分析結果および抗折力、硬度の測定結果を表1、表2に示す。本発明の方法による焼結体は、比較材に比べ、炭素量、酸素量とも低い値を示す。また、合金被覆を施した焼結体についても、その効果が現われている。この酸素量の低下にともない、抗折力は高い値を示し、逆に硬度は低い値を示し、Ti粉末に被覆を施すことにより脆性が改善されている。

#### 【0016】

##### 【表1】

## 機械的合金による本発明と比較材の材料特性

	Ti粉末平均 粒径 (μm)	試 料	被覆厚さ (μm)	混練時の最大 せん断応力(Pa)	射出成形時の最大 せん断応力(Pa)
比較例	8	Ti-0.5%Ni	0.03	$8 \times 10^4$	$6 \times 10^4$
本発明	8	Ti-2%Ni	1.2	$8 \times 10^4$	$6 \times 10^4$
本発明	8	Ti-6%Ni	2.4	$8 \times 10^4$	$2 \times 10^5$
比較例	8	Ti-15%Ni	5.2	$8 \times 10^4$	$2 \times 10^5$
比較例	8	Ti-0.5%Co	0.03	$8 \times 10^4$	$6 \times 10^4$
本発明	8	Ti-6%Co	2	$2 \times 10^5$	$6 \times 10^4$
比較例	8	Ti-6%Co	2	$8 \times 10^4$	$5 \times 10^5$
比較例	8	Ti-6%Co	-混粉	$8 \times 10^4$	$6 \times 10^4$
比較例	8	Ti-20%Co	5.8	$8 \times 10^4$	$6 \times 10^4$
本発明	28	Ti-5%Cu	1.9	$1 \times 10^5$	$2 \times 10^5$
本発明	28	Ti-5%Cu	1.9	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-5%Cu	-混粉	$8 \times 10^4$	$6 \times 10^4$
本発明	28	Ti-6%Ag	2.1	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-6%Ag	2.1	$5 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-6%Ag	-混粉	$8 \times 10^4$	$6 \times 10^4$
本発明	28	Ti-6%Au	1.9	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-6%Au	-混粉	$8 \times 10^4$	$6 \times 10^4$

	C 量 (%)	O 量 (%)	抗折力 (kg/mm <sup>2</sup> )	硬 度 Hv
比較例	0.5	0.8	108	353
本発明	0.2	0.3	184	210
本発明	0.2	0.3	195	230
比較例	0.5	0.8	110	411
比較例	0.4	0.7	115	322
本発明	0.2	0.3	180	198
比較例	0.6	0.8	116	370
比較例	0.6	0.9	96	365
比較例	0.5	0.8	102	385
本発明	0.3	0.4	170	241
本発明	0.3	0.4	177	233
比較例	0.7	0.9	110	381
本発明	0.2	0.3	193	184
比較例	0.6	0.9	120	379
比較例	0.6	0.9	99	376
本発明	0.2	0.3	179	206
比較例	0.7	0.9	112	394

## 機械的複合(合金被覆)による本発明と比較材の材料特性

	Ti粉末平均 粒径(μm)	試料	被覆厚さ (μm)	混練時の最大 せん断応力(Pa)	射出成形時の最大 せん断応力(Pa)
本発明	28	Ti-1%Ni-4%Ag	2.2	8×10 <sup>4</sup>	6×10 <sup>4</sup>
比較例	28	Ti-1%Ni-4%Ag	2.2	8×10 <sup>4</sup>	3×10 <sup>4</sup>
本発明	8	Ti-3%Ni-3%Co	2.6	8×10 <sup>4</sup>	6×10 <sup>4</sup>
比較例	8	Ti-3%Ni-3%Co	2.6	5×10 <sup>4</sup>	6×10 <sup>4</sup>
本発明	28	Ti-1%Ni-1%Co-1.5%Cu	1.5	8×10 <sup>4</sup>	6×10 <sup>4</sup>
本発明	28	Ti-1%Ni-1%Co-1.5%Cu-2%Ag	2.7	8×10 <sup>4</sup>	6×10 <sup>4</sup>

	C量 (%)	O量 (%)	抗折力 (kg/mm <sup>2</sup> )	硬度 Hv
本発明	0.2	0.3	185	204
比較例	0.6	0.9	106	379
本発明	0.3	0.4	168	221
比較例	0.7	0.9	115	385
本発明	0.3	0.4	177	230
本発明	0.2	0.3	181	216

## 【0018】実施例2

## メッキ法による実施例

種々の平均粒径のTi粉末にNi、Co、Cu、Ag、Auの群から選ばれた1種以上の金属の無電解メッキを施した。用いたメッキ液を表3に示す。メッキ時間を変化させることにより、メッキ厚さ0.03~6μmまでのメッキ粉末を作製した。メッキ厚さはメッキを施した粉末を樹脂に埋め込み、研磨を行なった後、走査型電子顕微鏡(SEM)による粉末断面の観察結果から求めた。次に、これらの被覆粉末を熱可塑性樹脂、ワックス、可塑剤からなる有機バインダーと加圧ニーダーにより表4の最大せん断応力で混練し、金属粉末射出成形用コンパウンドを作製した。インラインスクリュ式の射出成形機によって、このコンパウンドから55×10×3mmの抗折力試験片を表4の最大せん断応力で成形し

た。成形体は窒素中450℃まで48時間で昇温することにより脱脂を行ない、続いてアルゴンガス中で1200℃で2時間保持し、焼結を行なった。

【0019】比較材として、表4に示した最大せん断応力で混練、成形したものを同様に脱脂、焼結した。

【0020】以上の焼結体に対する炭素量、酸素量の分析結果および抗折力、硬度の測定結果を表4、表5に示す。本発明の方法による焼結体は、比較材に比べ、炭素量、酸素量とも低い値を示す。また、合金被覆を施した焼結体についても、その効果が現われている。この酸素量の低下にともない、抗折力は高い値を示し、逆に硬度は低い値を示し、Ti粉末に被覆を施すことにより脆性が改善されている。

## 【0021】

## 【表3】

## めっき条件

メッキ値	メッキ浴	メッキ温度
Ni	塩化ニッケル (30 g/l) 次亜リン酸ナトリウム (10 g/l) クエン酸ナトリウム (10 g/l)	90℃
Co	塩化コバルト (15 g/l) 次亜リン酸ナトリウム (10 g/l) クエン酸ナトリウム (10 g/l)	90℃
Cu	硫酸銅 (29 g/l) 炭酸水素ナトリウム (10 g/l) 酒石酸塩 (30 g/l) 水酸化ナトリウム (20 g/l) 37%ホルムアルデヒド (100 ml/l)	室温
Ag	硝酸銀 (10 g/l) アンモニア水 (100 g/l) 酒石酸ナトリウムカリウム (50 g/l)	室温
Au	塩化金 (5 g/l) 塩化ナトリウム (2.5 g/l) 酒石酸 (10 g/l) かせいソーダ (150 g/l) アルコール (200 ml/l)	室温

【0022】

【表4】

## メ 法による本発明と比較材の材料特性

	Ti粉末平均 粒径 (μm)	試 料	被覆厚さ (μm)	混練時の最大 せん断応力(Pa)	射出成形時の最大 せん断応力(Pa)
比較例	8	Ti-0.5%Ni	0.03	$8 \times 10^4$	$6 \times 10^4$
本発明	8	Ti-2%Ni	1.5	$8 \times 10^4$	$6 \times 10^4$
本発明	8	Ti-6%Ni	2.8	$2 \times 10^5$	$6 \times 10^4$
比較例	8	Ti-15%Ni	6	$8 \times 10^4$	$6 \times 10^4$
比較例	8	Ti-0.5%Co	0.04	$8 \times 10^4$	$6 \times 10^4$
比較例	8	Ti-6%Co	0.04	$3 \times 10^5$	$6 \times 10^4$
本発明	8	Ti-6%Co	2.7	$8 \times 10^4$	$2 \times 10^5$
比較例	8	Ti-6%Co	2.7	$3 \times 10^5$	$6 \times 10^4$
比較例	8	Ti-20%Co	5.8	$8 \times 10^4$	$6 \times 10^4$
本発明	28	Ti-5%Cu	2.6	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-5%Cu	2.6	$3 \times 10^5$	$6 \times 10^4$
比較例	28	Ti-5%Cu	2.6	$8 \times 10^4$	$4 \times 10^5$
本発明	28	Ti-6%Ag	2.4	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-6%Ag	2.4	$8 \times 10^4$	$4 \times 10^5$
本発明	28	Ti-6%Au	2.1	$1 \times 10^5$	$6 \times 10^4$
比較例	28	Ti-6%Au	2.1	$5 \times 10^5$	$6 \times 10^4$

	C 量 (%)	O 量 (%)	抗折力 (kg/mm <sup>2</sup> )	硬 度 Hv
比較例	0.5	0.8	115	354
本発明	0.2	0.3	185	206
本発明	0.2	0.3	189	225
比較例	0.5	1.1	98	393
比較例	0.4	0.7	116	315
比較例	0.4	0.7	120	320
本発明	0.2	0.3	183	189
比較例	0.6	0.9	94	355
比較例	0.5	0.7	19	390
本発明	0.3	0.4	188	233
比較例	0.7	0.9	106	368
比較例	0.7	0.9	116	380
本発明	0.2	0.3	196	190
比較例	0.7	1.1	97	392
本発明	0.2	0.3	190	200
比較例	0.7	0.9	126	384

【0023】

【表5】

	Ti粉末平均 粒径(μm)	試料	被覆厚さ (μm)	混練時の最大 せん断応力(Pa)	射出成形時の最大 せん断応力(Pa)
本発明	28	Ti-1%Ni-4%Ag	2.4	$8 \times 10^4$	$6 \times 10^4$
比較例	28	Ti-1%Ni-4%Ag	2.4	$8 \times 10^4$	$3 \times 10^4$
本発明	12	Ti-3%Ni-3%Co	2.8	$2 \times 10^4$	$6 \times 10^4$
比較例	12	Ti-3%Ni-3%Co	2.8	$5 \times 10^4$	$6 \times 10^4$
本発明	28	Ti-1%Ni-1%Co-1.5%Cu	1.8	$8 \times 10^4$	$2 \times 10^4$
本発明	28	Ti-1%Ni-1%Co-1.5%Cu-2%Ag	2.9	$8 \times 10^4$	$6 \times 10^4$

	C量 (%)	O量 (%)	抗折力 (kg/mm <sup>2</sup> )	硬度 Hv
本発明	0.2	0.3	190	209
比較例	0.5	0.8	120	382
本発明	0.3	0.4	153	236
比較例	0.7	0.9	112	391
本発明	0.3	0.4	169	245
本発明	0.2	0.3	177	220

【0024】

【発明の効果】以上詳しく説明したように、本発明は金属粉末射出成形用Ti粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法によって0.05~5μmの厚さに被覆し、混練、成形、脱脂、焼結することを特徴とし、また、金属粉末射出成形用粉末とTi系粉末の表面上に、Ni、Co、Cu、AgおよびAuの群から選ばれた1種以上の金属粉を機械的複合法またはメッキ法によって0.05~5μmの厚さの層に被覆したTi系粉末とバインダーとを、最大せん断応力 $2 \times 10^5$  Pa以下で混

練し、かつ、最大せん断応力 $2 \times 10^5$  Pa以下で射出成形し、脱脂、焼結することを特徴とする。

【0025】本発明により、被覆する金属粉末としてTiより炭素、酸素の元素との結合の弱い金属を表面に被覆するか若しくはこのTi粒子と有機バインダーとの混練時の最大せん断応力を $2 \times 10^5$  Pa以下にすることにより、金属粉末射出成形法による炭素量、酸素量の低いTi系合金焼結体を製造することが可能となり、Ti系合金の問題点である脆性改善に大きく寄与するものである。



D1

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(54) Title of the Invention: A method for the production of Ti-based alloy sintered compacts by means of the metal powder injection moulding method

5 (57) Abstract

Purpose:

To provide a method for the production of Ti-based alloy sintered compacts of which the brittleness is improved

Constitution:

10 Ti powder of which the surface has been coated with a metal such as Ni, Co, Cu, Ag, Au or the like and organic binder are kneaded with a maximum shear stress of not more than  $2 \times 10^5$  Pa, injection moulded at a maximum shear stress of not more than  $2 \times 10^5$  Pa, degreased and sintered.

15

## Scope of the Patent Claim

### [Claim 1]

A method for the production of Ti-based alloy sintered compacts by the metal powder injection moulding method, characterized in that one or  
5 more type metal powder selected from among the group comprising Ni, Co, Cu, Ag, Au is coated onto the surface of Ti powder using a mechanical compositing method to a thickness of from 0.05 to 5  $\mu\text{m}$  and kneaded, moulded, degreased and sintered.

### [Claim 2]

10 A method for the production of Ti-based alloy sintered compacts by the metal powder injection moulding method, characterized in that Ti-based powder where one or more type of metal selected from among Ni, Co, Cu, Ag and Au has been coated as a layer of thickness from 0.05 to 5  $\mu\text{m}$  on the surface of Ti-based powder using a mechanical compositing  
15 method or a plating method and a binder are kneaded with a maximum shear stress of not more than  $2 \times 10^5$  Pa, injection moulded with a maximum shear stress of not more than  $2 \times 10^5$  Pa, degreased and sintered.

## Detailed Description of the Invention

20 [0001]

### Industrial Field of Application

The invention concerns a method for the production of Ti-based alloy sintered compacts by means of the metal powder injection moulding method, and more precisely the invention concerns a method for the  
25 production of Ti-based alloy sintered compacts of which the brittleness is improved by means of a metal powder injection moulding method in which Ti-based powder of which the surface has been coated with Ni, Co, Cu, Ag or Au metal powder either as it is or together with an organic binder is kneaded with a specified maximum shear stress, degreased and sintered.

30 [0002]

### Prior Art

Ti alloys are characterized by having a high specific strength and excellent corrosion resistance and so they are used as materials for use in

aircraft and as corrosion resistant materials in chemical plants for example. However, their casting properties and their workability in terms of cutting for example are poor and so there are problems with the method of production and the production of Ti alloys is generally accomplished using the methods of powder metallurgy. In powder metallurgy, the demand for the production of Ti alloys by means of the metal powder injection moulding method with which the dimensional precision is excellent and with which it is possible to produce products which have a complex shape is increasing.

10 [0003]

The prevention of embrittlement is an especially important point in the production of Ti alloys and so the content of solid solution elements such as carbon and oxygen is reduced as far as possible. Furthermore, in the metal powder injection moulding method an organic binder is kneaded with the metal powder and the process then involves moulding the mixture and degreasing and sintering operations, but in those cases where active Ti-based powder is used the Ti-based powder reacts with the elements carbon and oxygen in the organic binder and large amounts of carbon and oxygen are included after the degreasing process. In the production of Fe-based alloys and stainless steels with the metal powder injection moulding method it is possible to get rid of the carbon and oxygen which are left behind after degreasing by means of a reaction of the carbon and oxygen during sintering (Japanese Unexamined Patent Applications Laid Open H2-290901 and H2-54701), but with Ti alloys the carbides and oxides of Ti are stable and so it is impossible to get rid of the carbon and oxygen during sintering and there is a problem in that the carbon and oxygen which are present after degreasing remain as they are as carbon and oxygen in the sinter.

25 [0004]

30

#### Problems to be Resolved by the Invention

The present invention is intended to resolve the abovementioned problems and, in more practical terms, it is intended to provide a method for producing the required sintered compacts in which any increase in the

solid solution element such as carbon and oxygen content which results in embrittlement of the material in the production of the Ti alloy and the introduction of carbon and oxygen into the Ti-based powder during kneading, moulding and degreasing in the metal powder injection moulding method are both forcibly prevented, and which is such that the layer which has been coated on the Ti-based alloy is not peeled away in the subsequent kneading and moulding processes.

[0005]

#### Means of Resolving These Problems

That is to say, the invention is characterized in that that one or more type metal powder selected from among the group comprising Ni, Co, Cu, Ag, Au is coated onto the surface of Ti powder using a mechanical compositing method to a thickness of from 0.05 to 5  $\mu\text{m}$  and kneaded, moulded, degreased and sintered, and it is also characterized in that Ti-based powder where one or more type of metal selected from among Ni, Co, Cu, Ag and Au has been coated as a layer of thickness from 0.05 to 5  $\mu\text{m}$  on the surface of Ti-based powder using a mechanical compositing method or a plating method and a binder are kneaded with a maximum shear stress of not more than  $2 \times 10^5$  Pa, injection moulded at a maximum shear stress of not more than  $2 \times 10^5$  Pa, degreased and sintered.

[0006]

The constitution and action of the means of this invention are described in detail below.

[0007]

#### Action

The average particle size of the Ti-based powder which is used in the invention is preferably within the range from 0.1 to 100  $\mu\text{m}$  from the viewpoints of the fluidity of the compound and the sintering properties of the powder. It is most desirably within the range from 1.0 to 50  $\mu\text{m}$ . The fluidity during injection improves as the powder particle size becomes smaller and the sintering properties are also good and so this is advantageous, but an enormous amount of energy is required to form very

fine powders of average particle size less than  $0.1\ \mu\text{m}$  and so this is inconvenient in practical terms. If the average particle size exceeds  $100\ \mu\text{m}$  then the fluidity at the time of injection moulding becomes poor and the sintering properties also decline, and the sinter density is not increased.

- 5 Furthermore, the Ti-based powder may be a powder which has been produced using any method of production such as a hydrogenation dehydrogenation powder or a gas atomizer powder.

[0008]

- 10 Ni, Co, Cu, Ag and Au which form weaker bonds with elements such as carbon and oxygen than Ti are used as coating metals, and by coating these to a thickness of from  $0.05$  to  $5\ \mu\text{m}$  on the Ti-based powder surface it is possible to suppress the ingress of carbon and oxygen into the Ti powder. If the coated thickness is less than  $0.05\ \mu\text{m}$  then it is impossible to cover the Ti-based powder surface uniformly and carbon and oxygen  
15 gain entry and it is impossible to produce a sintered compact which has a low carbon and a low oxygen content. Furthermore, if the coating exceeds a thickness of  $5\ \mu\text{m}$  then the ductility of the material is reduced by the increase in the alloying element content and the effect of the invention is not realized.

20 [0009]

- Any method, such as the mechanical compositing method and the plating method may, be used as the method of coating one or more type of meal selected from among the group comprising Ni, Co, Cu, Ag and Au on the Ti-based powder surface. It is carried out in the following way with the  
25 mechanical compositing method. Using a pulverizing machine such as an attriter, ball mill, vibration mill or angstrom mill, for example, the Ti-based powder and the coating powder are introduced into the pulverizing machine and a coating treatment is carried out for from 15 to 120 minutes. The operation is preferably carried out under vacuum, in an  $\text{N}_2$  atmosphere or  
30 in an inert gas atmosphere such as an Ar atmosphere in order to prevent the occurrence of oxidation. The added coating powder may be of one

type or of a plurality of types. Both non-electrolytic plating and electrolytic plating can be used as plating methods.

[0010]

Organic binders can be used in the metal powder injection moulding method. The known binders can be used. Kneading machines with which kneading can be carried out with a shearing action such as a pressure kneader, a plastomill, a roll mill, a Banbury mixer, a single screw mixing machine, a twin screw mixing machine or the like can be used for kneading, but kneading may also be carried out using a combination of two or more types of machine. No particular limitation is imposed upon the order of kneading and any order can be used. Furthermore, all of the binder component and the powder may be kneaded at the same time, or the powder may be introduced and kneaded after first kneading all of the binder component. Furthermore, a component comprising powder and binder may be kneaded first of all and then the remainder of the binder component may be added subsequently. However, the kneading is carried out in each type of kneading machine under conditions where the maximum shear stress during kneading is not more than  $2 \times 10^5$  Pa. The shear stress is preferably from  $1 \times 10^3$  Pa to  $2 \times 10^5$  Pa. It is not possible to knead the powder and binder together uniformly with a shear stress of less than  $1 \times 10^3$  Pa. If a shear stress which exceeds  $2 \times 10^5$  Pa is applied then the coating of the Ti-based powder peels away and it becomes impossible to suppress the ingress of carbon and oxygen, and it is impossible to obtain a sintered compact which has a low carbon content and a low oxygen content. The shear stress during kneading is measured using the method defined in the way indicated below. That is to say, a compound is kneaded at the prescribed kneading temperature and kneading time and the product of the shear velocity generated during kneading and the viscosity at the kneading temperature measured with a capillary rheometer is taken to be the shear stress during kneading.

[0011]

The moulding can be carried out using an injection moulding machine generally used for moulding thermoplastic materials. The



injection system may be of the plunger type, the plunger pre-plast type, the screw pre-plast type or the in-line screw type. However, the injection moulding is carried out under conditions such that the maximum shear stress which acts on the compound in the pre-plasticization stage or during injection is not more than  $2 \times 10^5$  Pa. If a shear stress above this level is applied then the coating of the Ti-based powder peels away and in the ingress of carbon and oxygen cannot be suppressed, and it is not possible to produce a sintered compact which has a low carbon content and a low oxygen content. The shear stress during injection moulding is measured using the method defined in the way indicated below. That is to say, the product of the viscosity of the compound at the injection moulding temperature measured with a capillary rheometer and the shear velocity generated during the preliminary plasticizing stage or injection is taken to be the shear stress.

[0012]

Degreasing is preferably carried out using the thermal degradation method in a non-oxidizing atmosphere or under reduced pressure in order to prevent the occurrence of oxidation. Sintering is carried out in a non-oxidizing atmosphere or under vacuum.

[0013]

### **Example 1**

#### **(1) Examples with the Mechanical Compositing Method**

Ti powder of the average particle size shown in Table 1 and one or more type of metal powder selected from the group comprising Ni, Co, Cu, Ag and Au which formed the coating material indicated in Table 1 were introduced into a high speed rotary ball mill (attriter) and subjected to a compositing treatment for 60 minutes at a rotation rate of 300 r.p.m. in an  $N_2$  atmosphere. WC was used for the pulverizing balls and the treatment was carried out with water-cooling. Coated powders with a coating thickness of from 0.03 to 5.8  $\mu m$  were prepared by adjusting the amount of coating powder added. The thickness of the coated material was obtained from the results of observing the powder cross section with a scanning electron microscope (SEM) after embedding powder which had been

subjected to the compositing treatment in a resin and grinding. These coated powders were then kneaded with an organic binder comprising thermoplastic resin, wax and plasticizer in a pressure kneader at the maximum shear stress shown in Table 1 to prepare compounds for metal powder injection moulding purposes. Tensile strength specimens measuring 55 x 10 x 3 mm were moulded from these compounds using an injection moulding machine at the maximum shear stress shown in Table 1. The mouldings were degreased by raising the temperature to 450°C in nitrogen for a period of 48 hours and then they were maintained at 1200°C for 2 hours in argon gas and sintering was carried out.

[0014]

As comparative materials, Ti powder and the same coating powders were mixed in a V-type blender and then kneading, moulding, degreasing and sintering were carried out in the same way to prepare sinters.

[0015]

The results of analyzing the carbon and oxygen contents and the measured results for the tensile strengths and hardnesses of the abovementioned sintered compacts are shown in Table 1 and Table 2. The sintered compacts obtained with the method of the present invention displayed low carbon contents and oxygen contents when compared with the comparative materials. Furthermore, sintered compacts where alloy coating had been carried out also revealed this effect. The tensile strength was seen to rise as the oxygen content fell and, conversely, the hardness exhibited a low value and the brittleness was improved by coating the Ti powder.

[0016]

Table 1

	Ti Powder Average Particle Size ( $\mu\text{m}$ )	Material	Coating Thickness ( $\mu\text{m}$ )	Maximum Shear Stress During Kneading (Pa)	Maximum Shear Stress During Injection Moulding (Pa)
Comparative Ex.	8	Ti -0.5% Ni	0.03	$8 \times 10^4$	$6 \times 10^4$
This Invention	8	Ti-2% Ni	1.2	$8 \times 10^4$	$6 \times 10^4$
This Invention	8	Ti-6% Ni	2.4	$8 \times 10^4$	$2 \times 10^5$
Comparative Ex.	8	Ti-15% Ni	5.2	$8 \times 10^4$	$2 \times 10^5$
Comparative Ex.	8	Ti-0.5% Co	0.03	$8 \times 10^4$	$6 \times 10^4$
This Invention	8	Ti-6% Co	2	$2 \times 10^5$	$6 \times 10^4$
Comparative Ex.	8	Ti-6% Co	2	$8 \times 10^4$	$5 \times 10^5$
Comparative Ex.	8	Ti-6% Co	Mixed powder	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	8	Ti-20% Co	5.8	$8 \times 10^4$	$6 \times 10^4$
This Invention	28	Ti-5% Cu	1.9	$1 \times 10^5$	$2 \times 10^5$
This Invention	28	Ti-5% Cu	1.9	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-5% Cu	Mixed powder	$8 \times 10^4$	$6 \times 10^4$
This Invention	28	Ti-6% Ag	2.1	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-6% Ag	2.1	$5 \times 10^5$	$6 \times 10^4$
Comparative Ex.	28	Ti-6% Ag	Mixed powder	$8 \times 10^4$	$6 \times 10^4$
This Invention	28	Ti-6% Au	1.9	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-6% Au	Mixed powder	$8 \times 10^4$	$6 \times 10^4$

	C Content (%)	O Content (%)	Tensile Strength ( $\text{kg/mm}^2$ )	Hardness Hv
Comparative Ex.	0.5	0.8	108	353
This Invention	0.2	0.3	184	210
This Invention	0.2	0.3	195	230
Comparative Ex.	0.5	0.8	110	411
Comparative Ex.	0.4	0.7	115	322
This Invention	0.2	0.3	180	198
Comparative Ex.	0.6	0.8	116	370
Comparative Ex.	0.6	0.9	96	365
Comparative Ex.	0.5	0.8	102	385
This Invention	0.3	0.4	170	241
This Invention	0.3	0.4	177	233
Comparative Ex.	0.7	0.9	110	381
This Invention	0.2	0.3	193	184
Comparative Ex.	0.6	0.9	120	379
Comparative Ex.	0.6	0.9	99	376
This Invention	0.2	0.3	179	206
Comparative Ex.	0.7	0.9	112	394

[0017]

**Table 2**

	Ti Powder Average Particle Size ( $\mu\text{m}$ )	Material	Coating Thickness ( $\mu\text{m}$ )	Maximum Shear Stress During Kneading (Pa)	Maximum Shear Stress During Injection Moulding (Pa)
This Invention.	28	Ti-1% Ni-4% Ag	2.2	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-1% Ni-4% Ag	2.2	$8 \times 10^4$	$3 \times 10^5$
This Invention	8	Ti-3% Ni-3% Co	2.6	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	8	Ti-3% Ni-3% Co	2.6	$5 \times 10^5$	$6 \times 10^5$
This Invention	28	Ti-1% Ni-1% Co-1.5% Cu	1.5	$8 \times 10^4$	$6 \times 10^4$
This Invention	28	Ti-1% Ni-1% Co-1.5% Cu- 2% Ag	2.7	$8 \times 10^4$	$6 \times 10^4$

	C Content (%)	O Content (%)	Tensile Strength ( $\text{kg/mm}^2$ )	Hardness Hv
This Invention	0.2	0.3	185	204
Comparative Ex.	0.6	0.9	106	379
This Invention	0.3	0.4	168	221
Comparative Ex.	0.7	0.9	115	385
This Invention	0.3	0.4	177	230
This Invention	0.2	0.3	181	216

5 [0018]

### Example 2

#### Examples with the Plating Method

Non-electrolytic plating of one or more metal selected from among Ni, Co, Cu, Ag and Au was carried out on Ti powders of various average particle sizes. The plating baths used were as shown in Table 3. Plated powders with plating thicknesses of from 0.03 to 6  $\mu\text{m}$  were produced by varying the plating time. The plating thickness of the coated material was obtained from the results of observing the powder cross section with a scanning electron microscope (SEM) after embedding powder which had been plated in a resin and grinding. These coated powders were then kneaded with an organic binder comprising thermoplastic resin, wax and plasticizer in a pressure kneader at the maximum shear stress shown in Table 4 to prepare compounds for metal powder injection moulding purposes. Tensile strength specimens measuring 55 x 10 x 3 mm were moulded from these compounds using an in-line screw type injection moulding machine at the maximum shear stress shown in Table 4. The mouldings were degreased by raising the temperature to 450°C in nitrogen

for a period of 48 hours and then they were maintained at 1200°C for 2 hours in argon gas and sintering was carried out.

[0019]

Compounds which had been kneaded and moulded with the maximum shear stress shown in Table 4 were degreased and sintered in the same way as comparative materials.

[0020]

The results of analyzing the carbon and oxygen contents and the measured results for the tensile strength and hardness of the abovementioned sintered compacts are shown in Table 4 and Table 5. The sintered compacts obtained with the method of the present invention displayed low carbon contents and oxygen contents when compared with the comparative materials. Furthermore, the sintered compacts where alloy coating had been carried out also revealed this effect. The tensile strength was seen to rise as the oxygen content fell and, conversely, the hardness exhibited a low value and the brittleness was improved by coating the Ti powder.

[0021]

**Table 3**

Plating	Plating Bath	Plating Temperature
Ni	Nickel chloride (30 g/l) Sodium hypophosphite (10 g/l) Sodium citrate (10 g/l)	90°C
Co	Cobalt chloride (15 g/l) Sodium hypophosphite (10 g/l) Sodium citrate (10 g/l)	90°C
Cu	Copper sulphate (29 g/l) Sodium bicarbonate (10 g/l) Rochelle salts (30 g/l) Sodium hydroxide (20 g/l) 37% Formaldehyde (100 ml/l)	Room Temperature
Ag	Silver nitrate (10 g/l) Aqueous ammonia (100 g/l) Sodium potassium tartrate (50 g/l)	Room Temperature
Au	Gold chloride (5 g/l) Sodium chloride (2.5 g/l) Tartaric acid (10 g/l) Caustic soda (150 g/l) Alcohol (200 ml/l)	Room Temperature

[0023]

**Table 5**

	Ti Powder Average Particle Size ( $\mu\text{m}$ )	Material	Coating Thickness ( $\mu\text{m}$ )	Maximum Shear Stress During Kneading (Pa)	Maximum Shear Stress During Injection Moulding (Pa)
This Invention.	28	Ti-1% Ni-4% Ag	2.4	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-1% Ni-4% Ag	2.4	$8 \times 10^4$	$3 \times 10^5$
This Invention	12	Ti-3% Ni-3% Co	2.8	$2 \times 10^5$	$6 \times 10^4$
Comparative Ex.	12	Ti-3% Ni-3% Co	2.8	$5 \times 10^5$	$6 \times 10^5$
This Invention	28	Ti-1% Ni-1% Co-1.5% Cu	1.8	$8 \times 10^4$	$2 \times 10^5$
This Invention	28	Ti-1% Ni-1% Co-1.5% Cu- 2% Ag	2.9	$8 \times 10^4$	$6 \times 10^4$

	C Content (%)	O Content (%)	Tensile Strength ( $\text{kg/mm}^2$ )	Hardness Hv
This Invention	0.2	0.3	190	209
Comparative Ex.	0.5	0.8	120	382
This Invention	0.3	0.4	153	236
Comparative Ex.	0.7	0.9	112	391
This Invention	0.3	0.4	169	245
This Invention	0.2	0.3	177	220

5 [0024]

Effect of the Invention

As described in detail above, the present invention is characterized in that one or more type of metal selected from among Ni, Co, Cu, Ag and Au is coated to a thickness of from 0.05 to 5  $\mu\text{m}$  using a mechanical  
10 compositing method of the surface of Ti powder for metal powder injection moulding purposes and the coated powder is kneaded, moulded, degreased and sintered and, moreover, it is characterized in that Ti-based powder where one or more type of metal selected from among Ni, Co, Cu, Ag and Au has been coated to a thickness of from 0.05 to 5  $\mu\text{m}$  using a  
15 mechanical compositing method or a plating method on the surface of Ti-based powder for metal powder injection moulding purposes and a binder are kneaded with a maximum shear stress of not more than  $2 \times 10^5$  Pa and then injection moulded with a maximum shear stress of not more than  $2 \times 10^5$  Pa, degreased and sintered.

20 [0025]

By means of the present invention it is possible to produce Ti-based alloy sintered compacts which have a low carbon content and a low oxygen content by the metal powder injection moulding method by covering the

- surface with a metal which has weaker bonding with the elements carbon and oxygen than Ti for the coated metal powder and setting the maximum shear stress to not more than  $2 \times 10^5$  Pa when kneading these Ti particles with an organic binder, and to provide a marked improvement in respect of
- 5 the brittleness which is a problem with Ti alloys.

[0022]

Table 4

	Ti Powder Average Particle Size (μm)	Material	Coating Thickness (μm)	Maximum Shear Stress During Kneading (Pa)	Maximum Shear Stress During Injection Moulding (Pa)
Comparative Ex.	8	Ti-0.5% Ni	0.03	$8 \times 10^4$	$6 \times 10^4$
This Invention	8	Ti-2% Ni	1.5	$8 \times 10^4$	$6 \times 10^4$
This Invention	8	Ti-6% Ni	2.8	$2 \times 10^5$	$6 \times 10^4$
Comparative Ex.	8	Ti-15% Ni	6	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	8	Ti-0.5%Co	0.04	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	8	Ti-6% Co	0.04	$3 \times 10^5$	$6 \times 10^4$
This Invention	8	Ti-6% Co	2.7	$8 \times 10^4$	$2 \times 10^5$
Comparative Ex.	8	Ti-6% Co	2.7	$3 \times 10^5$	$6 \times 10^4$
Comparative Ex.	8	Ti-20% Co	5.8	$8 \times 10^4$	$6 \times 10^4$
This Invention	28	Ti-5% Cu	2.6	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-5% Cu	2.6	$3 \times 10^5$	$6 \times 10^4$
Comparative Ex.	28	Ti-5% Cu	2.6	$8 \times 10^4$	$4 \times 10^5$
This Invention	28	Ti-6% Ag	2.4	$8 \times 10^4$	$6 \times 10^4$
Comparative Ex.	28	Ti-6% Ag	2.4	$8 \times 10^4$	$4 \times 10^5$
This Invention	28	Ti-6% Au	2.1	$1 \times 10^5$	$6 \times 10^4$
Comparative Ex.	28	Ti-6% Au	2.1	$5 \times 10^5$	$6 \times 10^4$

	C Content (%)	O Content (%)	Tensile Strength (kg/mm <sup>2</sup> )	Hardness Hv
Comparative Ex.	0.5	0.8	115	354
This Invention	0.2	0.3	195	206
This Invention	0.2	0.3	189	225
Comparative Ex.	0.5	1.1	98	393
Comparative Ex.	0.4	0.7	116	315
Comparative Ex.	0.4	0.7	120	320
This Invention	0.2	0.3	183	189
Comparative Ex.	0.6	0.9	94	355
Comparative Ex.	0.5	0.7	19	390
This Invention	0.3	0.4	188	233
Comparative Ex.	0.7	0.9	106	368
Comparative Ex.	0.7	0.9	116	380
This Invention	0.2	0.3	196	190
Comparative Ex.	0.7	1.1	97	392
This Invention	0.2	0.3	190	200
Comparative Ex.	0.7	0.9	126	384



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